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Basic Information about Carbenes

Nuriye Tuna Subasi

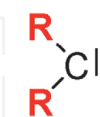
Abstract

In organic chemistry, good knowledge of the chemistry of reactive intermediates is very important in understanding organic chemistry, which has a systematic like mathematics. Having this information, it is possible to predict the reactions and the products to be formed on the reactive intermediates. Otherwise, it becomes impossible to learn organic chemistry, which has a very wide scope. This chapter of the book will be a guide that summarizes the essential information about carbene, one of the important reactive intermediates. It is planned to include the following sub-headings in this chapter: Carbene definition and properties, Nomenclature of carbenes, Structure and reactivity of carbenes, Carbene synthesis, Carbene reactions.

Keywords: carbenes, triplet and singlet carbenes, diazo compounds, carbene synthesis, carbene reactions

1. Introduction

Carbenes are neutral, divalent (two atoms attached to the central carbon atom) and highly reactive carbon intermediates generally written as " $R_2C:$ ". Carbenes, which have six electrons in their outer orbital, have a nonbonding pair of electrons and their formal charge is zero. They are short-lived and exhibit extreme reactivity because of electron deficiency.



carbene

$R = C, N, O, S, F, Cl, Br, I \dots$

The simplest carbene is the CH_2 compound and is called methylene, the term being first introduced during 19th century [1]. As early as 1835, Dumas [2] reported his attempts to prepare the parent carbene (CH_2) by dehydration of methanol. Actually at that time, the quadrivalency of carbon atom was not exactly established and for this reason many ancient chemist believed that methylene would be a stable compound, and various experiments were carried out to produce it. At the end of the 19th century, Curtius [3] and Staudinger [4] showed that carbenes, produced from diazo compounds or ketenes, were highly reactive species. In addition to this, carbenes became popular as transient species [5] in the 1940–1950s, when Doering [6] discovered the cyclopropanation reaction. Then the word carbene was first used by Woodward, Doering and Winstein at a meeting of the American Chemical Society in 1951.

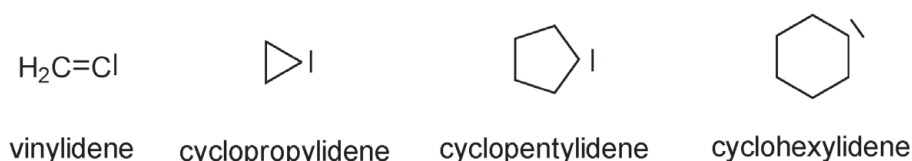
Carbenes are generally classified as triplet and singlet. As we will explain in detail later in singlet carbenes the two electrons are paired and the molecule is diamagnetic, while for triplet carbenes the two electrons are unpaired and the molecule is paramagnetic. Carbenes can be either linear or bent.

2. Nomenclature of carbenes

Today, the term carbene is used for divalent carbon species, and they are commonly referred to together with substituents. Substituents are given first, and the word carbene is added to the end.



If the divalent carbon atom is in a ring or the carbene electrons are on a carbon-carbon double bond carbon atom, these carbenes are named by the suffix *-ylidene* [7].



3. Structure and reactivity

Generally, carbenes have two bonding electrons (both in sp^2 -orbitals) and two non-bonding electrons. There are two classes of carbenes called singlet or triplet carbene depending on whether the non-bonding electrons are in the same or different orbitals, respectively as shown in **Figure 1**. Carbenes usually contain sp^2 hybridized carbon atoms according to the valence bond theory. Two of the three sp^2 -hybrid orbitals bond with their carbene substituents by covalent bonds and two vacant orbitals remain, consisting of the sp^2 -hybrid orbital and the p orbital. Two non-bonding carbene electrons must be placed in these vacant orbitals. If two electrons are placed in the same orbital, this carbene is called a singlet carbene, since the electron spins will be in the opposite directions. When electrons are placed in different orbitals, parallel spin will be preferred according to Hund's law, and the formed carbene is called triplet carbene [7–11].

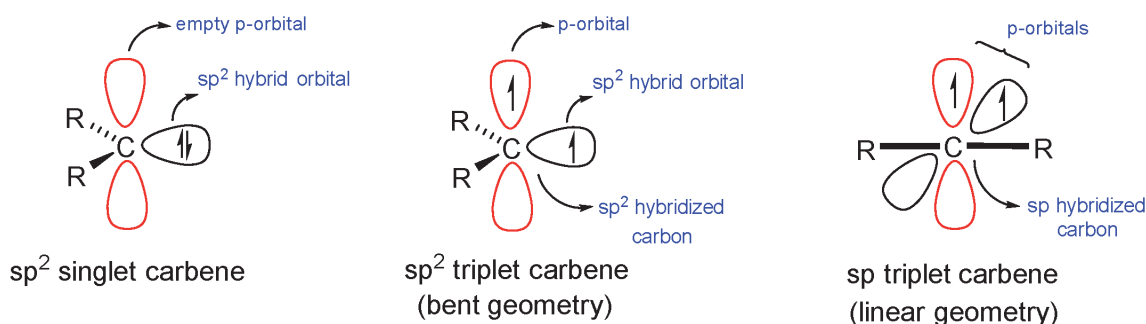


Figure 1.
Electronic structures of singlet and triplet carbene.

Triplet carbenes have an angular structure, as well as a linear structure. In carbene, which has a linear structure, the carbon atom to which the substituents are attached makes the sp² hybridization and there are two vacant p orbitals in the molecule. Since the energy levels of these orbitals will be equal, according to Hund's law, carbene electrons are placed in these orbitals one by one and carbene gains the triplet property [7–11].

Generally in most of the organic compounds, the singlet state is more stable than the triplet state. As a result the ground states of these molecules are singlet. In these molecules triplet state occurs only as excited or high energy level. On the contrary, studies show that carbenes usually have an angular structure and their electronic structure is triplet in the ground state because triplet carbenes have lower energy so they are more stable than singlet carbenes. Energy difference between singlet and triplet carbene is 8 kcal/mol.

The nature of substituents affects the electronic properties of carbenes. If the substituents attached to the carbene carbon are electron withdrawing groups, the carbene prefers the singlet structure. Electron withdrawing groups inductively stabilize the σ-orbital attached to the carbene carbon, increasing the energy difference between the σ- and π-orbital. Thus, electrons place in the σ-orbital, leaving the π-orbital empty. Conversely, if the substituents attached to the carbene carbon are electron donating groups via the σ-bond, the carbene prefers the triplet structure [7–11].

In addition, if the atoms attached to the carbene carbon have non-bonding electron pairs (nitrogen, oxygen, sulfur, halogen, etc.), these atoms easily donate their electrons to the vacant p-orbital of carbene. Thus, this π-donor atoms stabilize the singlet state by resonance structure and then carbenes prefer the singlet configuration in the ground state. For example, dichlorocarbene is singlet in the ground state. As shown in **Figure 2**, electrons on the chlorine atom are conjugated with the carbene atom, increasing the stability of the carbene [7–12].

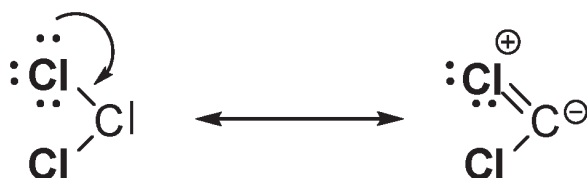


Figure 2.
 Stabilization of dichlorocarbene singlet state by π-donation (mesomeric effect).

Unstabilized carbenes usually have triplet ground states due to their stability, [9] but lone pair donating substituents can reverse this situation. As a consequence, electronic substituent effects, typically π-donation (such as -NR₂, -OR, -SR, -F, -Cl, -Br, -I) and π-acceptance (such as -COR, -SOR, -SO₂R, -NO, -NO₂) [13], as well as hyperconjugation (by alkyl groups) [14] and electronegative substituents [15] mainly stabilize the singlet state. Moreover, electropositive substituents with at least one atom having non-bonding electron pair give singlet carbene [16].

The nature of the substituents affect the chemical reactivity of carbenes as well as their electronic structure. Since carbenes are electron deficient intermediates (the carbon atom having only six electron in its outer shell), they show electrophilic behavior in their reactions. Naturally, when electron withdrawing groups are attached to these carbenes, the electrophilicity of the carbene increases. Nevertheless, if very strong π-donor substituents are attached to the carbene intermediate then it behaves as nucleophile in its reactions. For example, diaminocarbenes (**Figure 3**) are nucleophilic singlet carbenes because of π-donation of substituent [1, 7].

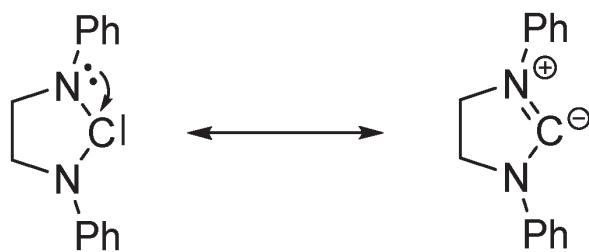


Figure 3.
Example of diaminocarbenes (nucleophilic singlet carbene).

Another example of nucleophilic singlet carbenes is the cycloheptatrienyldiene molecule. Since the vacant p-orbital located on the carbene atom participates in the delocalization of π -system of the seventh ring, the carbene electrons have to be placed in the sp^2 hybrid orbital on the ring plane. Therefore, cycloheptatrienyldiene is a singlet and nucleophilic carbene [1, 7].

It is not possible to observe carbenes under normal conditions. However, by using the matrix isolation method carbenes formed by photolysis of diazo compounds at 4–77 K in frozen argon or cyclohexane can be observed by IR or ESR (Electron Spin Resonance) spectroscopy [1]. Since ESR is a spectroscopic method based on electron spin, triplet carbenes can be observed with this method. Triplet carbenes, which act like diradicals, can be observed with ESR due to these properties. ESR not only clearly defines triplet carbenes, but also gives information about the molecular and electronic structures of carbenes [17–20]. For example, with this method, it was determined that triplet methylene and diphenylcarbene were angular and these angles were 136° and 142° , respectively.

Carbenes can be stabilized by steric or electronic effects [9]. As a result of the studies carried out in the light of this idea, some stable carbene molecules can be isolated at room temperature as shown in **Figure 4**. In 1988, Bertrand [21] et al reported the synthesis of the (phosphino)(silyl)carbene (first isolated carbene) **1** which can remain stable for weeks at room temperature. This compound, obtained by the decomposition of diazo compounds, was isolated by vacuum distillation (10^{-2} Torr) at $75\text{--}80^\circ\text{C}$ as a red oily material in 80% yield. It has all the typical reactivity associated with “classic” carbenes [22]. A few years later the first crystalline carbene was reported by Arduengo and co-workers [23]. This discovery catalyzed research activities of carbene. The 1,3-diadamantylimidazol-2-ylidene **2** can easily synthesized in 96% yield under an inert atmosphere even at room temperature. Bond angle of 1,3-diadamantylimidazol-2-ylidene, a colorless and crystalline compound with a melting point of 240°C , was determined as 102° by X-ray analysis. There are two main factors that stabilize this molecule. Nitrogen atoms attached to the carbene atom stabilize the carbene electronically, while adamantane groups attached to the nitrogen atoms make it sterically stable.

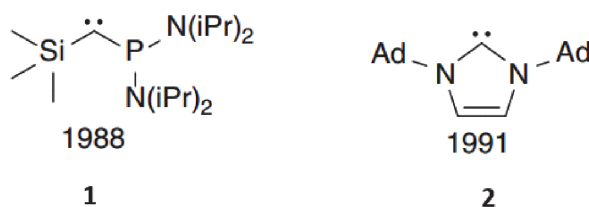


Figure 4.
The first isolated carbenes. *iPr* = isopropyl, *Ad* = adamantyl.

4. Generation of carbenes

The synthesis of carbene molecules is generally based on elimination and fragmentation reactions. Carbenes are formed as intermediate products when groups attached to the carbon atom are broken as a result of photolysis, thermolysis or reaction with metals.

4.1 Fragmentation reactions

Diazo compounds, tosylhydrazones, ketenes, three-membered carbon rings, strained alkenes and heterocyclic compounds are generally used as carbene precursors in fragmentation reactions.

4.1.1 Diazo compounds

Diazo compounds ($RR'C=N_2$), constitute a principal class of carbene precursors, known since the first preparation of ethyl diazoacetate by Curtius in 1883 [24]. Diazo compounds, which have 1,3-dipolar structures (**Figure 5a**), are generally converted to related carbenes by easily removing nitrogen gas when heated or photolyzed in aprotic solvents as shown in **Figure 5b**. This conversion has been proven by spectroscopic methods. The electronic spectrum of methylene produced in the gas phase by flash photolysis of diazomethane was recorded by Herzberg and Shoosmith [25]. Various metal complexes are used as catalyst for carbene formation to occur at low temperatures. Since diazo compounds are generally unstable and easily degradable compounds, they must be synthesized before each reaction.

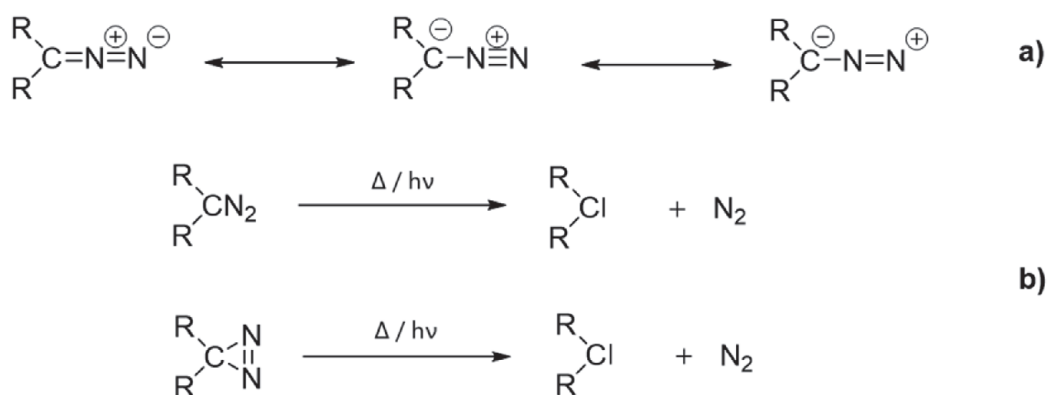


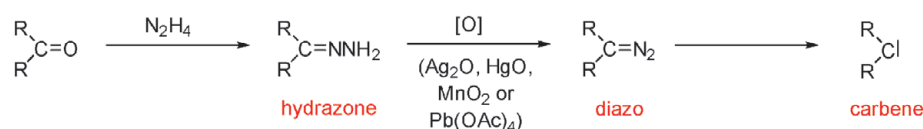
Figure 5.
(a) Resonance structure of 1,3-dipolar diazo compound. (b) Generation of carbene from diazo compounds.

Diazo compounds, which have a unique reactivity due to their 1,3-dipole and ylide structures, are useful synthetic products in organic synthesis. However, their large-scale use has been avoided due to their toxicity and unpredictable explosive behavior [26].

4.1.2 Tosylhydrazones

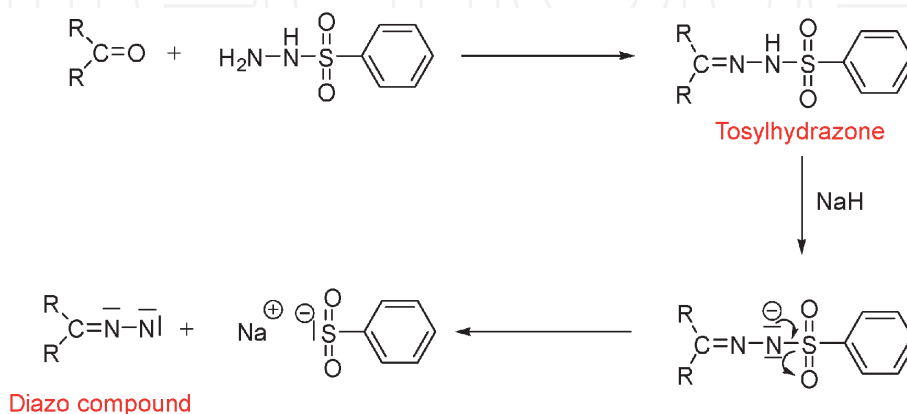
Where the diazo compound is somehow unstable and dangerous to use, it is usually better to use a diazo precursor. The simplest and most common compounds used for this are hydrazones. Ketones and aldehydes easily react with hydrazine to form hydrazone compounds. The oxidation of hydrazones with metal salts such as Ag_2O , HgO , MnO_2 , $Pb(OAc)_4$ gives the diazo compound (**Figure 6**).

The most widely known and used carbene precursors are tosylhydrazones which are prepared from the reaction of aldehydes and ketones with p-toluenesulphonyl hydrazide.

**Figure 6.**

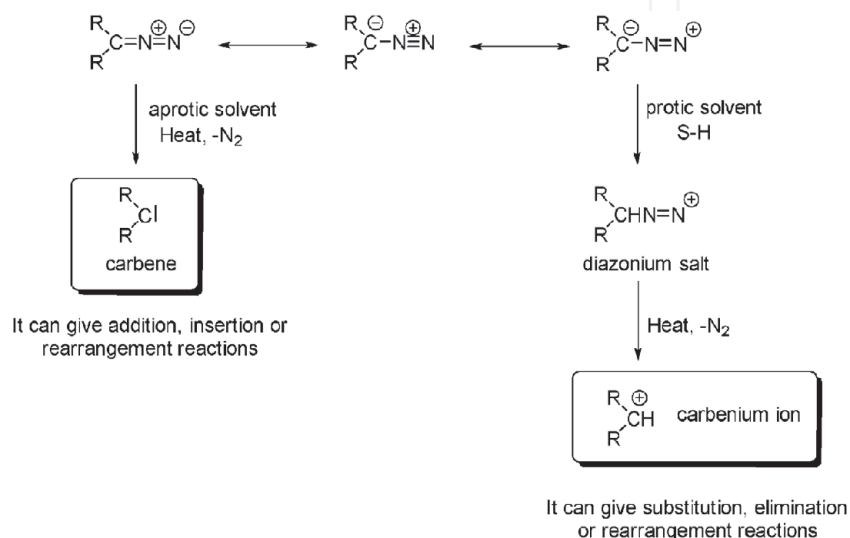
Generation of carbenes from hydrazones compound.

p-Toluenesulfonylhydrazones (tosylhydrazones) of aldehydes and ketones undergo base-catalyzed thermal decomposition with loss of p-toluenesulfinate to give intermediate diazo compounds [27]. This method is called the Bamford-Stevens reaction (**Figure 7**).

**Figure 7.**

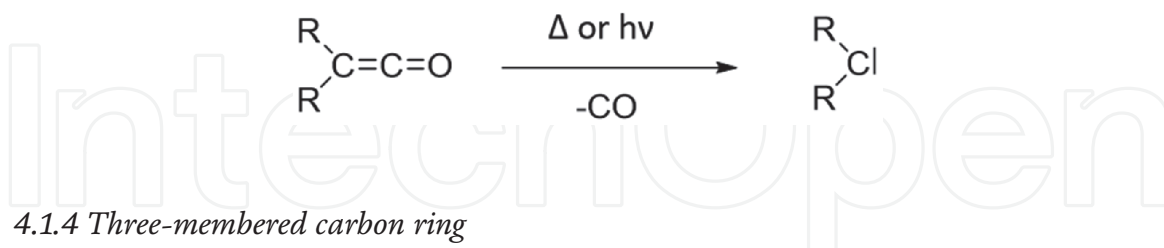
Bamford-Stevens reaction.

When the N-H proton in the tosylhydrazone molecule is removed with a base such as NaH or NaOCH₃, the formed anion is stabilized by the tosyl group. Therefore, the resulting salt can be isolated and stored for a long time. This salt can be converted to carbene by heating at any time in situ. After the nitrogen gas is separated, alkene formation is observed as a result of 1,2-hydrogen shift. When the alkene formation mechanism was examined comprehensively, it was found that the products formed may vary depending on the reaction conditions [28]. In the Bamford-Stevens reaction, if the decomposition of the tosylhydrazone salt is done in aprotic solvents, carbene is formed by the removal of nitrogen gas. The resulting carbene usually forms an alkene as a result of 1,2-hydrogen shift. However, if the salt is decomposed in protic solvents, the diazonium salt is formed first. Diazonium salts, especially the aliphatic ones, are not stable, they turn into carbenium ions by removing nitrogen gas.



4.1.3 Ketenes

Ketenes can eliminate CO molecule on thermolysis or photolysis to generate carben. Since ketenes are not readily available precursor and polymerize under the reaction conditions, they are not widely used. Ketene has been used extensively to generate CH₂.



4.1.4 Three-membered carbon ring

Three-membered rings that have a high ground state energy due to steric strain often decompose to give carbene intermediates by heating or irradiation. For example; photolysis of 1,1-dichloro-2-phenylcyclopropane apparently gives CCl₂ and photolytic decomposition of oxiranes yield arylcarbenes and related species as shown in **Figure 8**.

Substituted phenyloxiranes provide convenient precursors for substituted arylcarbenes, such as diphenylcarbene [29], phenylmethylcarbene [30], cyanophenylcarbene [31, 32], and methoxycarbonylphenylcarbene [33]. Selective cleavage was observed with unsymmetrical precursors, the thermodynamically more stable isomer appears to be favored.

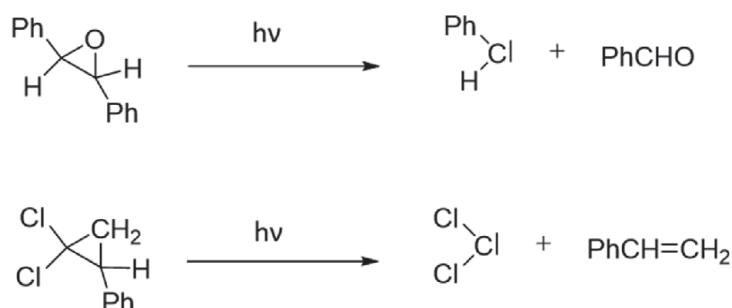


Figure 8.
 Generation of carbene from cyclopropanes and epoxides.

The most useful carbene precursors of the three-membered ring are diazirines. Diazirines, the cyclic isomers of diazoalkanes, also decompose under the influence of heat and light to give carbenes [34–37]. As shown in **Figure 9**, they are prepared from ketones by reaction with ammonia and chloramine followed by oxidation of the resulting diaziridine. This method is quite widely used especially for halocarbenes.

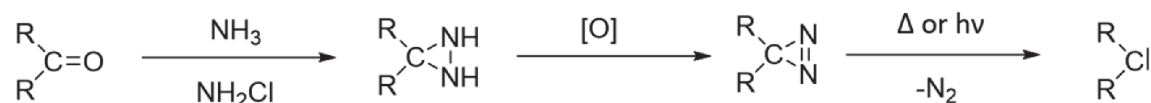


Figure 9.
 Preparation and decomposition of diazirines.

4.1.5 Strained alkenes

If the alkene is extremely sterically hindered then the π-bond is weakened due to the substantially reduced p–p overlap and distortion from planarity. As a result, the

ground state energy is raised and then dissociation to carbenes become possible by heating. The well-known example of this process is the reversible dissociation of tetranaphth-1-ylethene into bis(naphth-1-yl) carbene at 250°C [38] (**Figure 10**).

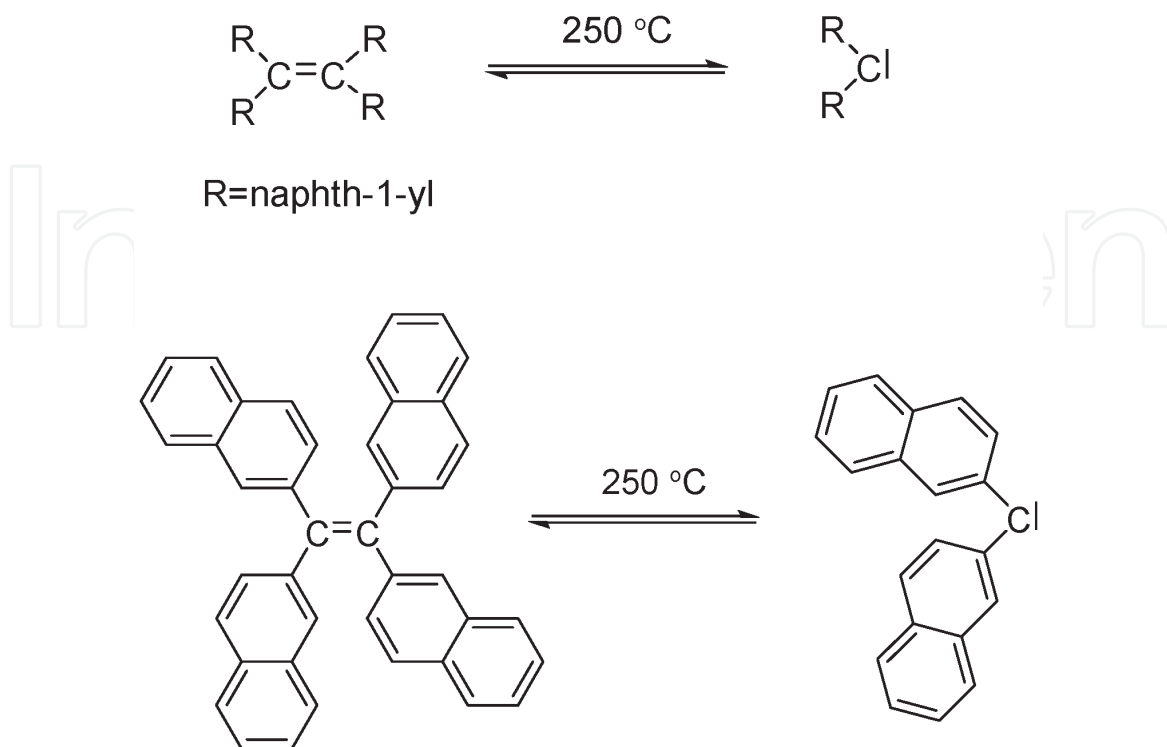


Figure 10.
Thermal dissociation of tetranaphth-1-ylethene.

4.1.6 Heterocycles

Various five-membered heterocyclic compounds decompose to give carbenes by heating or irradiation (**Figure 11**). The decomposition of 1,5-dihydro-1,3,4-oxadiazoles give carbenes at about 80°C with loss of nitrogen followed by the carbonyl fragment.

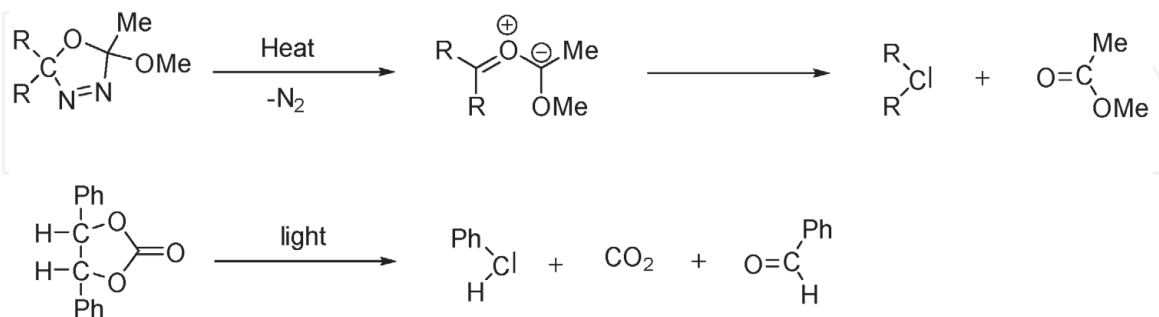


Figure 11.
Fragmentation of five-membered heterocycles to carbenes.

4.2 α -Elimination

The hydrolysis of chloroform in basic medium was probably the first reaction in which intermediate carbene formation was suggested by Geuther [39]. The investigation the mechanism of this reaction by Hine and co-workers initiated the modern era of carbene chemistry in the early 1950s [40–42]. In the basic environment, the acidic proton of chloroform separates and trichloromethyl anion is formed.

Dichlorocarbene is formed as a result of the removal of the chloride anion from the carbanion. By hydrolysis of dichlorocarbene in aqueous media, carbon monoxide is formed (**Figure 12**). These types of reactions are called α -elimination reactions because the hydrogen and chlorine released in the formation of carbene are attached to the same carbon atom.

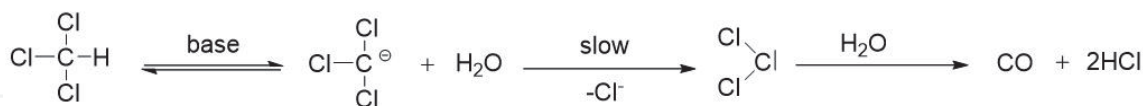


Figure 12.
 α -Elimination reactions.

In experiments with aprotic solvents and strong bases, it was determined that carbene was formed and added to the double bond electrons to form cyclopropane derivatives as shown in **Figure 13**. This reaction is the best method for cyclopropane synthesis in organic chemistry.

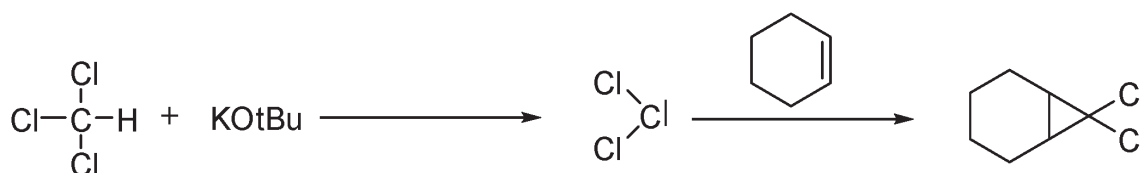


Figure 13.
 Cyclopropane synthesis.

Before the reaction, the solvent used must be dried very well. Because the water in the environment can easily react with the carbene formed, and it also reacts with the base in the environment and completely prevents the formation of carbenes. However, in Makosza, a study carried out in a two-phase system, showed that carbenes were formed in the presence of phase transfer catalysts in aqueous medium and added to double bonds (**Figure 14**) [43].

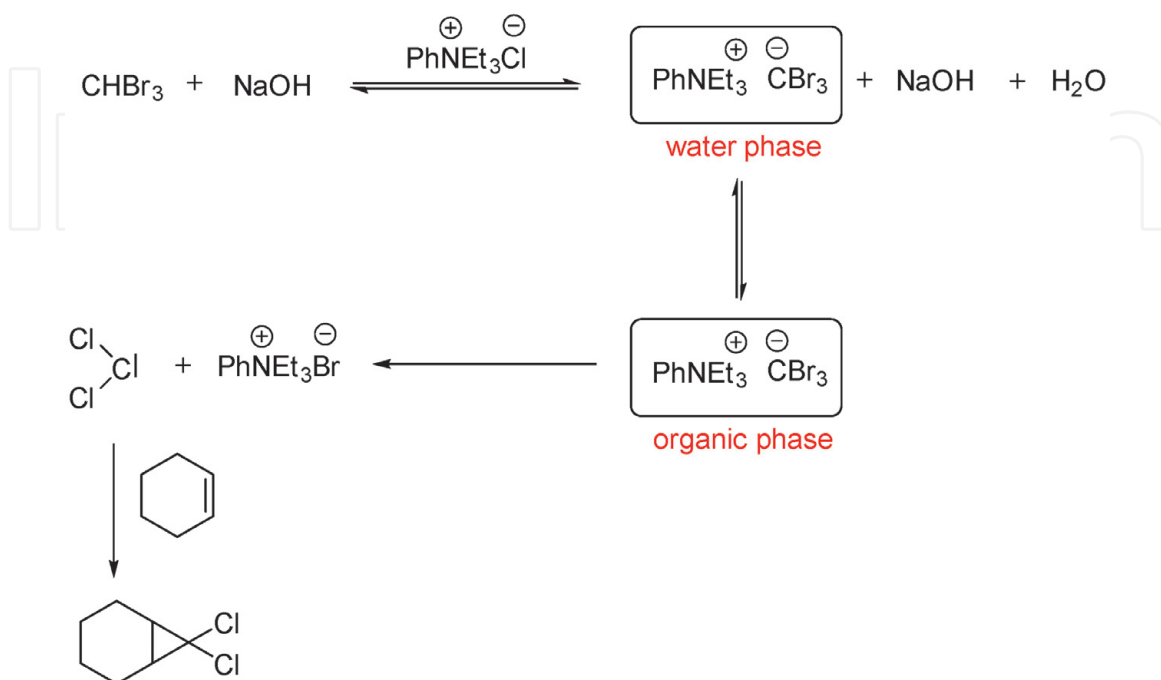


Figure 14.
 Carbene formation in a two-phase system.

Since the reaction is between two phases, effective mixing is very important for this reaction. Although the reaction is carried out in the presence of water, the carbene is generated and reacts in the organic phase.

4.2.1 Simmon-Smith reaction

It is not possible to synthesize methylene carbene by the α -elimination method. However, there are methods that form methylene carbene adducts. The most commonly used method is the reaction of alkenes with diiodomethane in the presence of zinc. As a result of the reaction, cyclopropane compounds are formed (**Figure 15**) [44, 45].

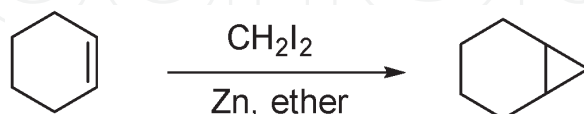


Figure 15.
Simmon-Smith reaction.

During this reaction, methylene carbene is not formed in the free form. First, zinc and diiodomethane react to form a carbenoid intermediate, which acts as a carbene. Later, since this product is unstable, it transforms into zinc iodide by transferring the methylene group to the double bond as shown in **Figure 16** [46].

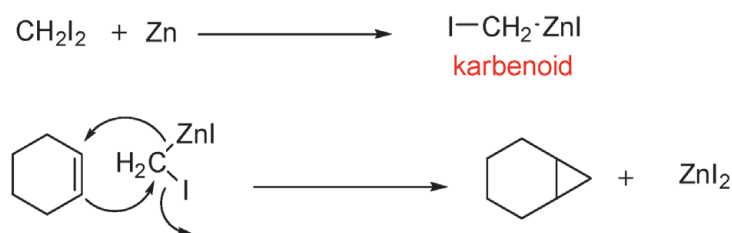


Figure 16.
Mechanism of Simmon-Smith reaction.

5. Carbene reactions

Singlet and triplet carbene exhibit different reactivity. Singlet carbenes generally participate in reactions as either electrophiles or nucleophiles. Singlet carbenes which have unfilled p-orbitals should be electrophilic. Triplet carbenes can be considered as diradicals and participate in stepwise radical additions. Triplet carbenes must pass through an intermediate with two unpaired electrons, while single carbenes can react in a single concerted step. Because carbenes have two modes of reactivity, singlet methylene gives stereospecific reactions where as triplet methylene gives stereoselective reactions [47].

Carbenes are highly reactive intermediate due to electron deficiency. Carbenes react instantly in various ways in the environment where they are formed. Carbene reactions are classified under four main groups.

5.1 Cycloaddition reaction of carbenes

Since carbenes generally react electrophilically, they give a $[2 + 2]$ cycloaddition reaction with double bonds to form cyclopropane compounds (**Figure 17**). This

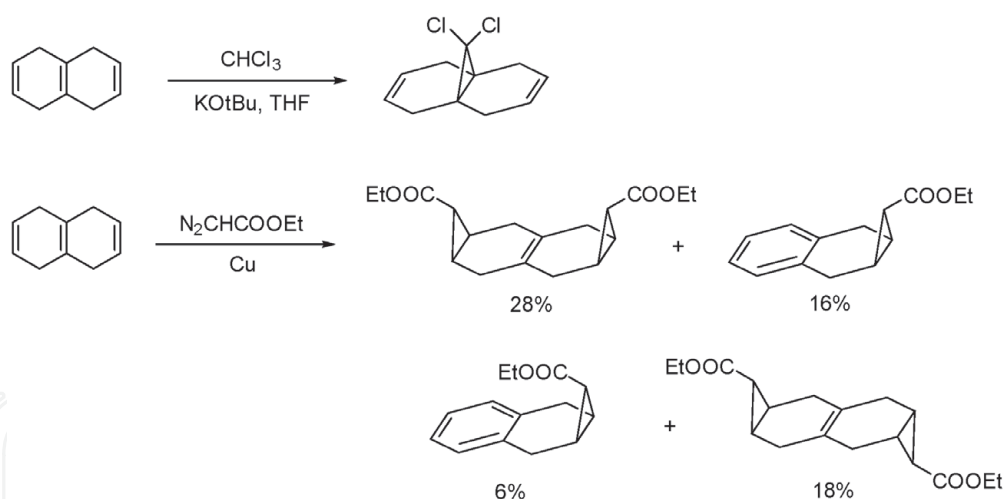


Figure 17.
 Cycloaddition reaction of carbenes.

method, the most characteristic reaction of carbene intermediates, has now been widely used as a synthetic route to cyclopropane since 1954 [6].

According to the theory proposed by Skell and Woodworth [47], singlet carbenes are added the double bonds simultaneously in a single step. The opening of double bond electrons and the formation of new carbon–carbon bonds occur simultaneously. On the other hand, triplet carbenes are not added in double bonds in a single step because this addition is forbidden by orbital symmetry. Triplet carbenes form cyclopropane compounds by adding double bonds as a result of a multi-step reaction.

Since carbenes are generally electrophilic compounds, they prefer double bonds where the electron density is high when adding systems that contain more than one double bond. In particular, singlet carbenes (dihalocarbenes) show more regioselective properties as they are more stable. For example, in the isotetralin compound, which has two different double bonds, dihalocarbene selectively adds the central double bond, although it has a steric hindrance. However, the more reactive ethoxycarbonylcarbene cannot act selectively due to its shorter lifetime and adds the double bonds located on the outer part of the molecule as shown below.



5.2 Dimerization reaction of carbenes

When carbenes cannot find a reagent that can react in the environment in which they are formed, they dimerize to fill the electron gap in their outer orbitals and turn into olefins (**Figure 18**).



Figure 18.
 Dimerization reaction of carbenes.

5.3 Insertion reaction of carbenes

Another characteristic reaction that carbenes give to become stable is that carbenes insert between C-H or C-C bonds (**Figure 19**).



Figure 19.
Examples of carbene insertion reaction.

Methylene, when there is no double bond to react it is not selective and insert into a random C-H bond in the liquid phase. Methylene acts selectively in the gas phase and preferentially inserts into tertiary C-H bonds as shown in **Figure 20**.

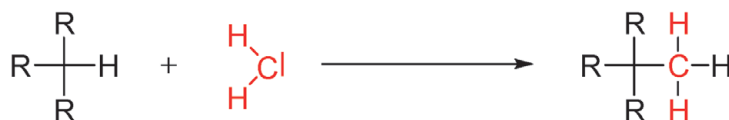


Figure 20.
Insertion of methylene.

The electronic structure of carbene plays an important role in the insertion reactions (**Figure 21**). Singlet carbenes generally insert into bonds in a single step with retention of configuration. The situation is different with triplet carbenes. Since triplet carbenes act as radicals, they first abstract hydrogen from the C-H bond and form two new radicals. With the combination of these radicals, a new C-C bond is formed. Meanwhile, as the radical configuration undergoes isomerization, a racemic mixture is formed as a result of the reaction. In the insertion of triplet carbenes, tertiary carbon-hydrogen bonds are primarily preferred because they form stable radicals.

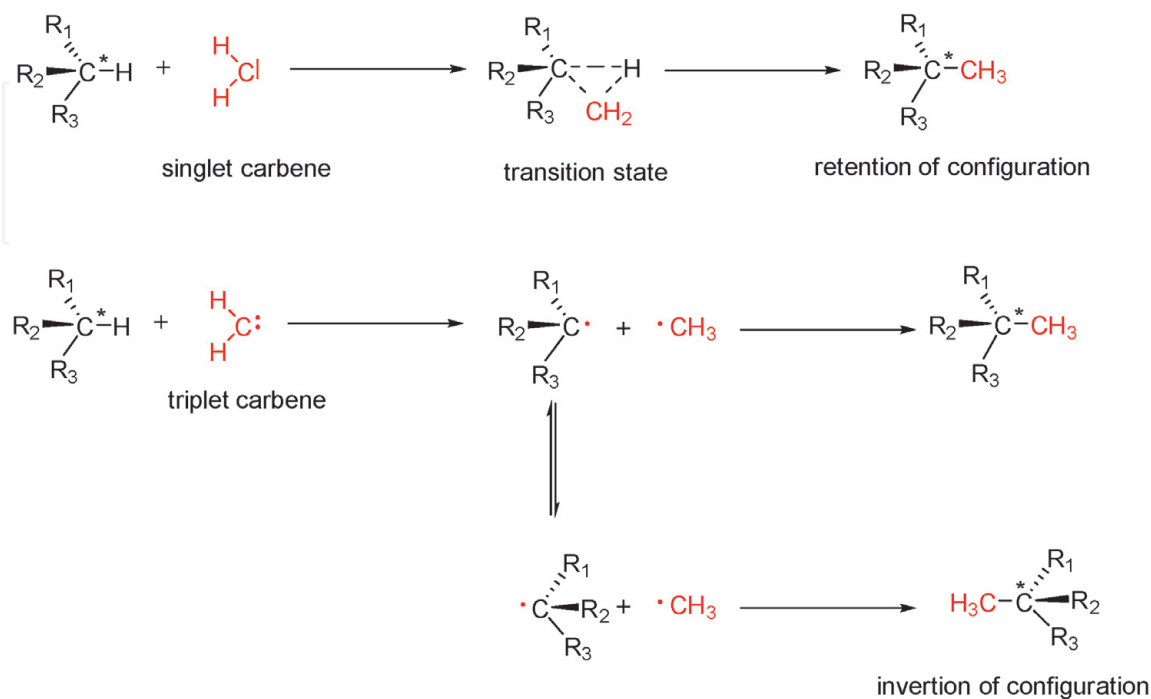


Figure 21.
Mechanism of singlet and triplet carbene in the insertion reaction.

5.4 Rearrangement of carbenes

Since carbenes are electron-deficient intermediates with an empty p-orbital, an atom or group on the neighboring carbon migrates to the electron-deficient center and undergoes easy rearrangement with simultaneous formation of a new C=C bond. Usually this rearrangement is called 1,2-shift, and it usually involves the migration of a hydrogen atom, since the order of migrating ability is: $H > \text{aryl} > \text{alkyl}$. This hydrogen shift is also considered as the intramolecular addition of the carbene to the adjacent C-H bond.

The best known carbene rearrangement is the rearrangement of diazoketones to ketenes. In this reaction, called Wolff rearrangement, α -diazoketo compounds primarily form α -ketocarbene by removing nitrogen gas thermally, photochemically, or in the presence of various metals. When the -R group electrons attached to the carbonyl group migrate to the carbene center, the carbene electrons form a double bond with the carbonyl carbon and ketene is formed. Later, ketenes react with water and turn into carboxylic acids [48]. According to the experiments, the Wolff rearrangement proceeds according to a concerted mechanism in which the migration occurs at the same time as the leaving group and the leaving nitrogen group and the migrating alkyl group should be in antiperiplanar conformation as shown in **Figure 22**.

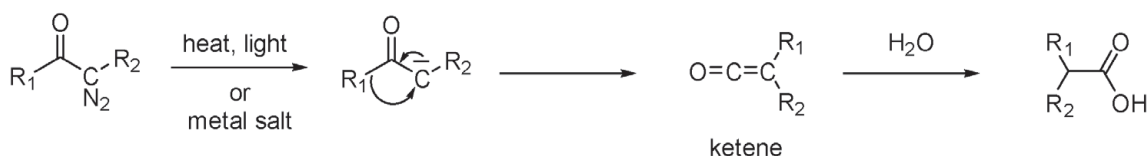


Figure 22.
 Wolff rearrangement.

When Wolff rearrangement is applied to cyclic systems, a ring reduction reaction occurs if the carbene located at the α -position to the carbonyl group is formed in a ring (**Figure 23**).

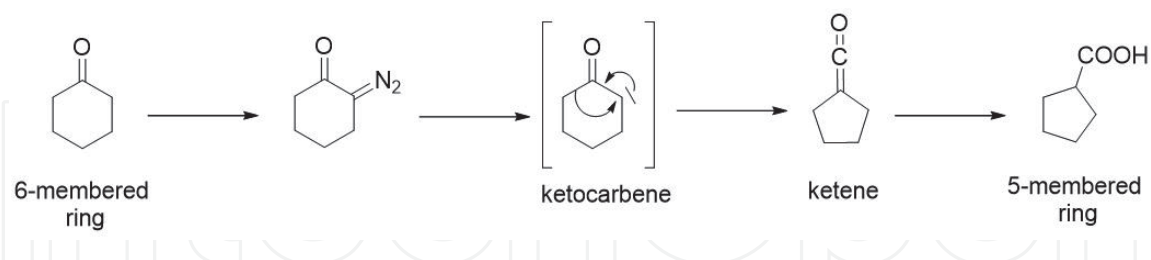


Figure 23.
 Ring reduction reaction in the cyclic system.

If the carbene is attached to the cyclic structure as a substituent, then a ring expansion reaction occurs (**Figure 24**).

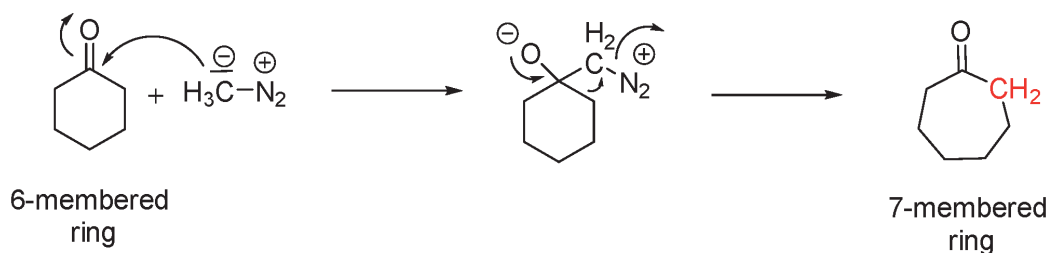


Figure 24.
 Ring expansion reaction in the cyclic system.

6. Use of carbenes in organic synthesis

6.1 Example 1

Preparation of tetracyclic cyclopropapyrroloindole, an analogue of the mitosene antitumor agent, involves an intramolecular carbene addition to an alkene (**Figure 25**).

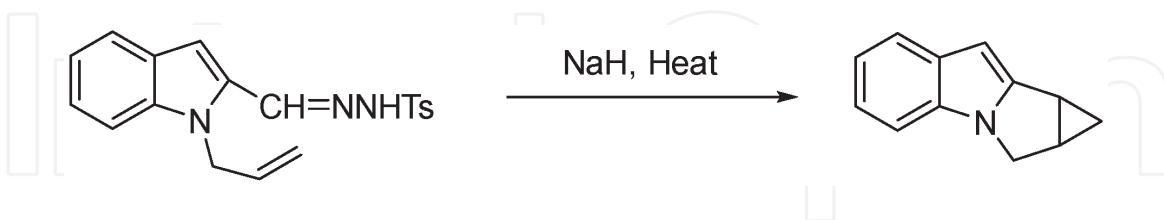


Figure 25.
Intramolecular carbene addition in the synthesis of tetracyclic indole.

6.2 Example 2

Cyclopentanes are prepared using intramolecular C-H insertions. The reactions involve the rhodium (II) catalyzed decomposition of α -diazo- β -keto esters as shown in **Figure 26**.

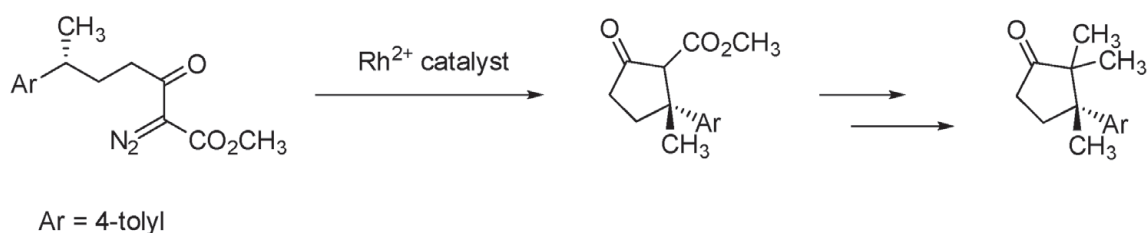


Figure 26.
Synthesis of cyclopentanones by intramolecular C-H insertion reaction.

6.3 Example 3

The β -lactam antibiotics are synthesized by using carbene reactions. This example as shown in **Figure 27** involves a Wolff rearrangement of a diazoketone to effect a ring contraction of five-membered ring.

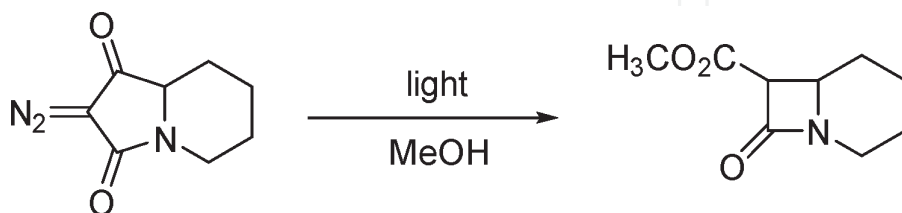


Figure 27.
Carbene reaction in the synthesis of β -lactam antibiotics.

6.4 Example 4

This example involves intramolecular O-H insertion reaction to synthesize heterocyclic compound (**Figure 28**).

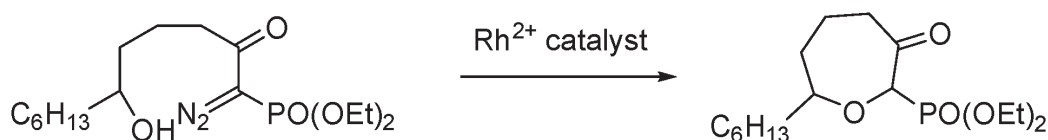


Figure 28.
Intramolecular O-H insertion.

6.5 Example 5: Arndt-Eistert reaction

Chain extension in carboxylic acid. Diazomethane is one of the reagents used to extend the chain in carboxylic acids. Carboxylic acids are converted to acid chlorides and treated with diazomethane without isolation to form α -diazoketones. The formed diazoketone easily turns into ketenes when heated. Finally, ketene reacts with water and gives carboxylic acid (**Figure 29**).

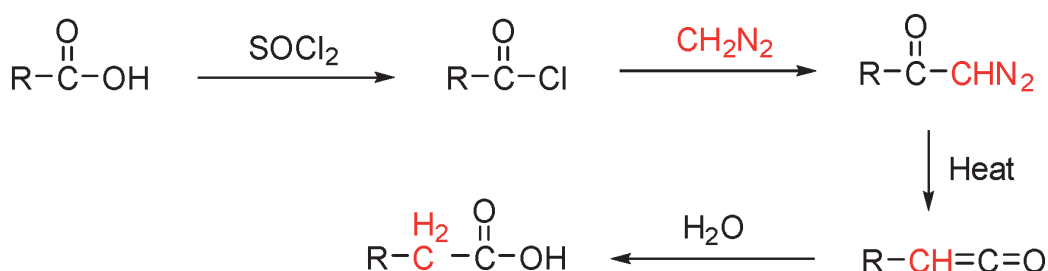


Figure 29.
Chain extension in carboxylic acid by using diazomethane.


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